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RADIATION BY HYDROGEN, CARBON
MONOXIDE AND NITROGEN

By
JAMES SAMUEL OWENS

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE UNIVERSITY OF MICHIGAN

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The Quenching of Mercury Resonance Radiation by Hydrogen, Carbon Monoxide and Nitrogen

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An investigation was made of the dependence upon the temperature of the quenching of mercury resonance radiation by hydrogen, carbon monoxide and nitrogen. The quenching by hydrogen was effectively independent of the temperature from 473°K to 973°K, but that by carbon monoxide and by nitrogen decreased with increasing temperature. This decrease was somewhat more marked in nitrogen than in carbon monoxide. These results show that the metastable 2^3P_0 state of the mercury atom is involved in the quenching by carbon monoxide and by nitrogen, but not appreciably in the quenching by hydrogen. The quenching by hydrogen may be accounted for by a reaction involving the dissociation of the hydrogen

molecule by collision with a 2^3P_1 mercury atom, followed in a certain small fraction of the cases by the probable excitation by collision with a second 2^3P_1 atom of the mercury hydride molecule so produced. The effective cross sections for energy transfer in the first process at the different temperatures are given. The quenching by carbon monoxide and by nitrogen may be accounted for by the transition $2^3P_1 \rightarrow 2^3P_0$ of the mercury atoms at gas collisions, by the return of some of the 2^3P_0 atoms to the 2^3P_1 state at subsequent gas collisions, and by the reduction of the remainder of them by several distinct processes to the 1^1S_0 state. The effective cross sections for the different processes are given.

INTRODUCTION

SINCE the introduction of the concept of "Collisions of the second kind" by Klein and Rosseland¹ many attempts have been made under different conditions to evaluate both the probabilities of such collisions and the accompanying "effective cross sections for energy transfer."

From kinetic theory, the action cross section, q , for a collision may be interpreted as the product $\pi S_{12}^2 \gamma$, where S_{12} is the sum of the effective radii of the colliding molecules and γ is the probability that the collision will result in a transfer of energy between the molecules at the distance S_{12} apart. Neither S_{12} nor γ , but only the product $S_{12}^2 \gamma$, hereafter denoted by σ^2 and called the effective cross section, can be obtained directly from experiment. Also, according to modern quantum mechanics a "collision radius" cannot be distinguished physically from a "collision probability." Therefore only the quantity σ^2 will be sought in the various types of collisions.

The values obtained for these probabilities and effective cross sections depend to some extent upon the experimental conditions and to a large extent upon the theoretical treatment of the data

as is shown by the results of the several analyses of the experimental observations of Stuart.²

Zemansky³ applied Milne's⁴ theory of the diffusion of resonance radiation, as modified by impacts of the second kind, to Stuart's data and found that a constant quenching efficiency could not be ascribed to each gas. Later, by means of a method more nearly suited to the requirements of Milne's theory, he⁵ investigated the quenching by a number of gases. He assumed that at the gas pressures used only the quenching process D (Fig. 1) was present for H_2 and O_2 , and only the primary quenching process E (Fig. 2) for CO , CO_2 , H_2O , and N_2 . From his experimental results he calculated a quantity σ_E^2 , an "effective cross section for quenching." This σ_E^2 is an effective average over all the cross sections accompanying the various quenching transitions.

Modern quantum mechanics⁶ has shown that the probability of energy exchange taking place at a collision depends upon the nature both of the colliding molecules and of the collision. The

² Stuart, *Zeits. f. Physik* **32**, 262 (1925); Foote, *Phys. Rev.* **30**, 288 (1927); Gaviola, *Phys. Rev.* **33**, 309; **34**, 1049; **34**, 1373 (1929); **35**, 1226 (1930); Mitchell and Zemansky, *Resonance Radiation and Excited Atoms* (1934).

³ Zemansky, *Phys. Rev.* **31**, 812 (1928).

⁴ Milne, *J. Lond. Math. Soc.* **I**, 40 (1926).

⁵ Zemansky, *Phys. Rev.* **36**, 919 (1930).

⁶ Kallmann and London, *Zeits. f. physik. Chemie* **B2**, 207A (1929); Morse and Stueckelberg, *Ann. d. Physik* **9**, 579 (1931); Stueckelberg, *Helv. Phys. Acta* **5**, 370 (1932).

¹ Klein and Rosseland, *Zeits. f. Physik* **4**, 46 (1921).

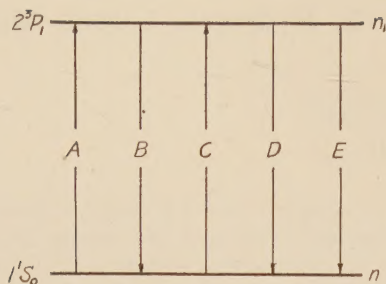


FIG. 1.

Transition processes of the mercury atom.

FIG. 1. Transitional diagram for the quenching by hydrogen.

- A—Absorption of $\lambda 2437$
- B—Spontaneous emission of $\lambda 2537$
- C—Reabsorption of $\lambda 2537$ within the mercury vapor.
- D—Dissociation of the hydrogen molecule by collision with a 2^3P_1 mercury atom.
- E—Excitation by collision with a second 2^3P_1 mercury atom of the mercury hydride molecule produced by D.

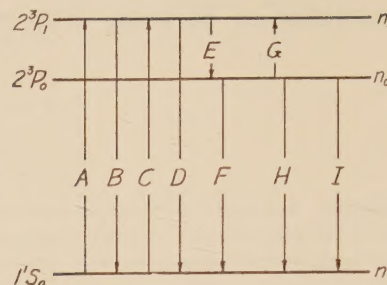


FIG. 2.

FIG. 2. Transitional diagram for the quenching by carbon monoxide and by nitrogen.

- A—Absorption of $\lambda 2537$
- B—Spontaneous emission of $\lambda 2537$
- C—Reabsorption of $\lambda 2537$ within the mercury vapor.
- D, E, F, G—Transitions of the mercury atoms produced by collisions with gas molecules.
- H—Transition of the 2^3P_0 mercury atom independent of the gas pressure, probably mercury molecule formation.
- I—Diffusion to the walls

nature of the collision depends primarily upon whether or not the transition of the excited molecule is optically allowed. Thus, in order for a quenching cross section to have more meaning than that of a kind of average one over the whole reaction, the actual processes taking place must be determined and a cross section calculated for each. No attempt to do this was made in any of the work mentioned above.

Samson⁷ studied the effect of temperature and of nitrogen pressure upon the decay of the afterglow of mercury resonance radiation in a mixture of mercury vapor and nitrogen. He took into account all the transition processes shown in Fig. 2 with the exception of H, and evaluated the "effective temperature cross section," which corresponds to σ_E^2 , for each process involving the collisions of excited mercury atoms with nitrogen molecules. Thus his values of effective cross sections have more meaning than any of the previous ones.

Upon the basis of the present experimental work, the quenching by hydrogen is taken to be a two-step reaction involving, as most important, the processes A, B, C, D and E in Fig. 1. The processes A, B, C, E, F, G, H and I in Fig. 2 are the ones used in the analysis of the quenching by carbon monoxide and by nitrogen. Effective cross sections are calculated for each process.

⁷ Samson, Phys. Rev. **40**, 940 (1932).

EXPERIMENTAL APPARATUS AND METHOD

The purpose of this experiment was to determine the type of reaction taking place between the excited mercury atoms and the foreign gas molecules by an investigation of the dependence of the quenching upon both the foreign gas pressure and the temperature.

The apparatus assembly was similar to that of Stuart.² The primary $\lambda 2537$ radiation from a special source was absorbed by mercury vapor at a pressure of 0.28 mm in a quartz cell. The resonance radiation which passed back through the incident window of the cell in a direction nearly parallel to that of the primary radiation was photographed.

The experimental cell was a quartz cylinder, 5.3 cm long and 3.5 cm in diameter, with plane quartz windows sealed on each end. It was connected to the liquid mercury source for the mercury vapor by an electrically heated quartz tube. The cell was enclosed in an electric furnace, provided with quartz windows. The temperature of the furnace could be accurately controlled up to 1070°K. The temperature of the liquid mercury source for the mercury vapor in the cell was held at 100°C by means of a thermostatic relay.

Two important improvements over the technique of Stuart were utilized, *viz.*, a constant primary light source and an improved method of

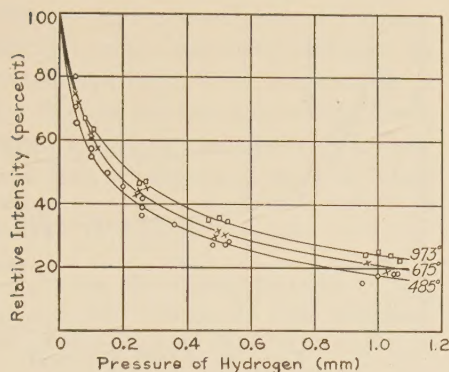


FIG. 3.

FIG. 3. Quenching by hydrogen. The curves are drawn from the theory and the plotted points represent experimental observations.

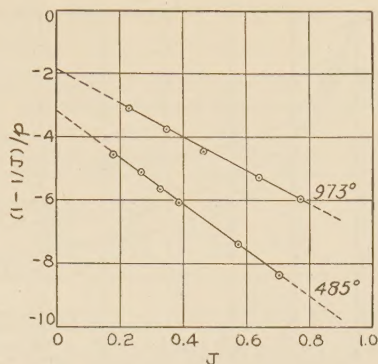


FIG. 4.

FIG. 4. Quenching by hydrogen. $(1 - 1/J)/p$ as a function of J .

intensity calibration of the photographic plates. The light source was a 30 m.a. glow discharge in a mixture of argon at 8.0 mm pressure and mercury vapor at 0.0004 mm pressure. The low mercury vapor pressure insured a very narrow $\lambda 2537$ line having a strong core, thus eliminating the necessity for a resonance lamp. The variation in the intensity of the $\lambda 2537$ line over a period of twelve hours was found to be less than one percent. A chlorine filter placed between the source and the resonance cell absorbed all the radiation from $\lambda 2600$ to $\lambda 4358$,⁸ thus preventing the stepwise excitation of the 2^3P_2 state.

Plate blackenings, obtained with a self-recording microphotometer of the Moll type, were translated into light intensities by the use of a step-diaphragm as described by Hansen.⁹

Great care was taken to insure extreme purity of the gases used. Hydrogen was admitted to the system by diffusion through an electrically heated platinum cylinder. Nitrogen and carbon monoxide were generated on an auxiliary system, transferred to the quenching system, and carefully purified by conventional means. Subsequent tests showed that both the latter gases were spectroscopically pure.

The experimental procedure was as follows: A photograph was taken with pure mercury vapor in the resonance vessel. Then a series of photographs were taken on the same plate with varying pressures of foreign gas, each pressure change being made very slowly, and the mercury vapor

pressure allowed to reach equilibrium before the following exposure. The temperature was kept constant during this time. Then a Hansen calibration pattern was photographed on the plate. This entire procedure was repeated for a series of temperatures of the resonance vessel from 473°K to 973°K.

Tests were made of the effects of variations in all of the experimental operations involved and showed that the probable experimental error did not exceed two percent for the procedure finally adopted. This high degree of accuracy was essential in order that the determination of the processes taking place in the quenching by hydrogen should be significant.

EXPERIMENTAL RESULTS

The experimental results are given in Tables I, II and III and in Figs. 3 to 6. The latter are curves showing the relative intensity J of the resonance radiation as a function of the foreign gas pressure p in mm of mercury. The plotted points were experimentally determined and the curves are drawn in accordance with the theory given below.

For hydrogen, Fig. 3, the results show that, in the temperature range investigated, the quenching by hydrogen is nearly independent of the temperature, while the quenching by carbon monoxide and by nitrogen decreases as the temperature is increased. This variation with temperature is more marked in nitrogen than in carbon monoxide. A brief investigation of the

⁸ Oldenberg, *Zeits. f. Physik* 29, 328 (1924).

⁹ Hansen, *Zeits. f. Physik* 29, 356 (1924).

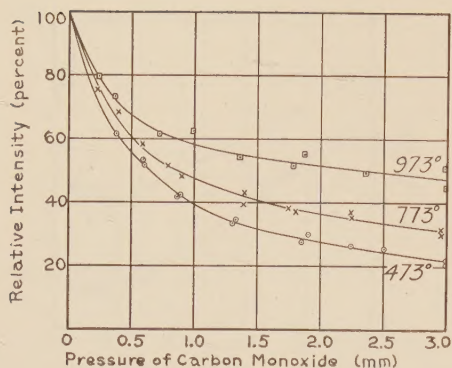


FIG. 5. Quenching by carbon monoxide.

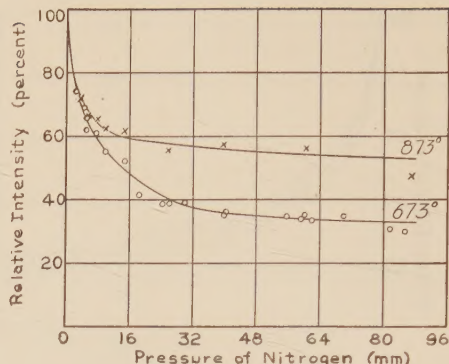


FIG. 6. Quenching by nitrogen.

quenching by nitrogen at 973°K indicated that the intensity of the resonance radiation decreased only to 85 percent of its original value even at a pressure of 90 mm of nitrogen. This result is in qualitative agreement with that of Cario and Franck.¹⁰

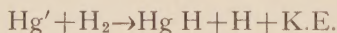
DISCUSSION AND INTERPRETATION OF RESULTS

Quenching by hydrogen

Upon the basis of the results of Franck and Cario,¹¹ the dissociation of the hydrogen molecule has always been regarded as the fundamental process in the quenching of mercury resonance fluorescence by hydrogen. Several types of reactions involving this dissociation have been advanced,¹² of which the two-step process postulated by Beutler and Rabinowitsch¹³ is the most probable.

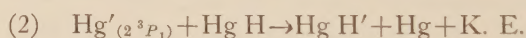
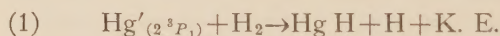
Since the quenching by hydrogen was found to be practically independent of the temperature, the effect of the mercury metastable 2^3P_0 state is negligible. Otherwise the quenching action should markedly decrease with increasing temperature due to the rapid increase with temperature of the reverse transition $2^3P_0 \rightarrow 2^3P_1$.

Heretofore, the hydrogen quenching reaction has been simply assumed to comprise only the one step.



However, from the quenching experiments one may determine whether there occurs a one-step reaction involving only one excited mercury atom or a two-step reaction, each step having a definite probability, involving two excited mercury atoms. This latter type of process proved to be the most probable on the basis of the excellent agreement between the theoretical curves obtained from it and the experimental quenching curves.

The calculation of J as a function of p is carried out on the basis of a two-step reaction:



The statistical processes are shown in Fig. 1.

n, n_1 = concentrations of the mercury atoms in the 1^1S_0 and 2^3P_1 states, respectively.

n is approximately the total concentration of the mercury atoms.

p = pressure of hydrogen in mm of mercury.

A = Einstein coefficient of spontaneous emission of $\lambda 2537$.

$B = AK$, where K is a constant proportional to the intensity of the incident radiation.

$\rho(\nu)d\nu$ = radiation density of a frequency between ν and $\nu + d\nu$ within the $\lambda 2537$ line.

$b(\nu)\rho(\nu)d\nu dt$ = probability that a 1^1S_0 atom will absorb a quantum in the frequency range between ν and $\nu + d\nu$ in time dt .

k_1 = number of effective collisions per second per excited atom at 1 mm hydrogen pressure producing transition D in Fig. 1.

$k_2 n_1^2$ = number of transitions per second at 1 mm hydrogen pressure corresponding to transition E in Fig. 1.

In the steady state,

$$dn_1/dt = 0 = Bn + n \int_0^\infty b(\nu)\rho(\nu)d\nu - An_1 - pk_1 n_1 - pk_2 n_1^2.$$

¹⁰ Cario and Franck, *Zeits. f. Physik* **37**, 619 (1926).

¹¹ Franck and Cario, *Zeits. f. Physik* **11**, 161 (1922).

¹² Compton and Turner, *Phil. Mag.* **48**, 360 (1924); Hulthen, *Zeits. f. Physik* **32**, 32 (1925).

¹³ Beutler and Rabinowitsch, *Zeits. f. physik. Chemie* **B8**, 403A (1930).

If we assume, as did Samson,⁷ that $\rho(\nu)$ at any point is chiefly due to the radiating atoms in its vicinity, we may represent the absorption term by Ln_1 , where L is an unknown constant. Then $P=A-L$ is the "resultant radiation coefficient" for the cell and each volume element in it. Then

$$0 = Bn - (P + pk_1 + pk_2n_1)n_1.$$

If $n_1^{(p)}$ and $n_1^{(o)}$ are the concentrations of the 2^3P_1 atoms in the presence and absence, respectively, of hydrogen, the ratio of the intensity I of the resonance radiation at any given hydrogen pressure to the intensity I_0 in pure mercury vapor is then

$$J = \frac{I}{I_0} = \frac{n_1^{(p)}}{n_1^{(o)}} = \frac{-(P + pk_1) + [(P + pk_1)^2 + 4pk_2AKn]^{1/2}}{2pk_2(AK/P)n}. \quad (1)$$

Although it is impossible to carry out a rigorous calculation for P for the present experimental apparatus, an approximate value for it may be obtained by consideration of the absorption coefficient of the mercury vapor for both the primary and resonance $\lambda 2537$ radiation and of the geometry of the apparatus. This value is $P = 0.2A = 1.82 \times 10^6$. The use of this same value at all the temperatures may be justified by the fact that at all the temperatures all of the incident light quanta are absorbed. The only effect of temperature change is to change slightly the depth of penetration of the incident light.

By means of (1) the values of the k_1 and k_2K may be obtained from the quenching data. The values taken for these quantities are average ones obtained from all the quenching data at each temperature. The effective cross section Σ_1^2 for the first process is obtained by equating the total number of collisions of the second kind per cm^3 per second experimentally determined to the total number of collisions within the distance Σ_1 given by a Maxwellian distribution of velocities.⁷ Hence

$$k_1 = (2N\Sigma_1^2/p_1)(2\pi kT/\mu)^{1/2} \quad (2)$$

where μ = reduced mass for mercury and hydrogen; T = absolute temperature; k = Boltzmann's constant; N , p = hydrogen concentration and

pressure, respectively. The results are given in Table I.

TABLE I. Values of k_1 , Σ_1^2 and k_2K for the quenching of mercury resonance radiation by hydrogen.

$T^\circ\text{K}$	$k_1 \times 10^{-6}$ from (1)	$\Sigma_1^2 \times 10^{16}$ from (1)	$k_2K \times 10^{10}$ from (1)	$k_1 \times 10^{-6}$ from curves	$\Sigma_1^2 \times 10^{16}$ of curves	$k_2K \times 10^{10}$ of Fig. 4
485	5.80	4.06	4.78	5.74	4.02	4.77
530	5.85	4.28	4.92	5.91	4.33	4.88
675	4.87	4.02	5.39	4.82	3.97	5.62
973	3.47	3.44	6.91	3.44	3.41	6.86

Confirmatory evidence that the quenching by hydrogen is a two-step reaction is obtained by plotting the quantity $(1 - 1/J)/p$ as a function of J .^{*} If the quenching is a one-step reaction, this curve should be a horizontal straight line with the constant value of $(1 - 1/J)/p = -k_1/P$. If it is a two-step reaction, this curve should be a straight line with intercept $-k_1/P$ at $J=0$ and slope $-k_2AKn/P^2$. The present experimental data plotted in this manner gave excellent straight lines of the latter type as shown in Fig. 4. The constants calculated from these curves are shown in the last three columns of Table I. The close agreement between the constants obtained by these two methods indicates the accuracy with which they were determined.

Since the quenching by hydrogen does apparently decrease slightly with increase of temperature, this fact might be attributed to the presence of the metastable 2^3P_0 state of mercury in the quenching reaction. However, this state has not been considered in the analysis of the quenching by hydrogen for several reasons. First, the experimental results show that any influence of this state upon the quenching must be very slight. Second, the energy of the 2^3P_0 atom, as well as that of the 2^3P_1 atom, is sufficient to dissociate the hydrogen molecule. Third, the inclusion of the effect of this state in the analysis so complicates the equations that an accurate solution becomes impossible, and, in view of its small effect, consideration of this state was omitted.

Quenching by carbon monoxide and by nitrogen

Since the quenching by carbon monoxide and by nitrogen decreases with increasing temperature and that by hydrogen is effectively independent of the temperature, there is an essential difference between the quenching reactions in the

^{*} This method was suggested by Professor A. E. Ruark.

two cases. This difference is due to the differences in their dissociation energies and in their critical potentials.

The primary process in the quenching by carbon monoxide and by nitrogen must be the reduction of the 2^3P_1 mercury atom to the 2^3P_0 metastable state by collision with a gas molecule. The energy difference, 0.218 volt, between these states is given to the gas molecule, and probably is transformed into vibrational energy.

If all the metastable atoms so produced were returned to the normal state by gas collisions or by diffusion to the walls, the quenching process should be that of a one-step reaction. However, the experimental data point to the occurrence of another process which partially neutralizes the effect of the quenching collisions. This process is taken to be the return of 2^3P_0 atoms to the 2^3P_1 state by gas collisions.

A priori, the transition $2^3P_0 \rightarrow 2^3P_1$ of the mercury atom may be produced by either one or both of the following types of collisions: (A) Collisions of the first kind with high speed gas molecules; (B) Collisions of the second kind with gas molecules having vibrational energy. The fraction of all collisions in which there is sufficient energy to produce the transition $2^3P_0 \rightarrow 2^3P_1$ is, for the two cases:

$$(A) \quad F_a = (1 + \epsilon/kT)e^{-\epsilon/kT}, \quad (3)$$

where ϵ is the energy difference between the 2^3P_1 and 2^3P_0 states.¹⁴

$$(B) \quad F_b = e^{-E/kT}, \quad (4)$$

where $E(\geq \epsilon)$ is the energy of a vibrational state of the gas (this will be the first vibrational state of nitrogen or carbon monoxide). For both gases, $F_b < F_a$. In fact $F_b < 0.2F_a$ from 291°K to 973°K.

The quenching action never entirely disappears at high temperatures because of the return of some metastable atoms to the normal state by diffusion to the walls, by gas collisions,¹⁵ or by processes independent of the pressure of the foreign gas. Since the effect of the first two of these processes should be less in nitrogen than in carbon monoxide, the quenching action should more nearly disappear in nitrogen. This fact was experimentally observed.

¹⁴ Tolman, *Statistical Mechanics*, The Chemical Catalogue Company, New York.

¹⁵ Gaviola, *Phil. Mag.* **6**, 1167 (1928).

The general expression derived for the quenching by carbon monoxide and by nitrogen is similar to that of Magliano and Gaviola¹⁶ and gives at high pressures essentially the same expression as does an adaptation of Samson's⁷ theory to quenching. The statistical processes are shown in Fig. 2.

n, n_1, n_0 = concentrations of mercury atoms in the 1^1S_0 , 2^3P_1 , and 2^3P_0 states, respectively.

N = concentration of foreign gas molecules.

k_1, K_1, k_0, K_0 = numbers of effective collisions per second per excited atom at 1 mm gas pressure producing the respective transitions E, D, G, F shown in Fig. 2.

$H_0 n_0$ = number of $2^3P_0 \rightarrow 1^1S_0$ transitions, corresponding to H in Fig. 2, per second produced by any processes independent of the foreign gas pressure.

$dn_0/(p+p_0)$ = loss per cm³ per second of 2^3P_0 atoms by diffusion to the walls, corresponding to transition I in Fig. 2.

p = pressure of foreign gas in mm of mercury.

p_0 = pressure of mercury vapor in mm of mercury.

The diffusion of 2^3P_1 atoms is not considered because their natural lifetime is too short to permit them to reach the walls before radiating.

Here, as in the quenching by hydrogen, $P = A - L$ is the resultant radiation coefficient. In the steady state by equating the number of transitions both to and from the 2^3P_1 and the 2^3P_0 states, we have

$$Bn + pk_0n_0 = (P + pk_1 + pK_1)n_1, \quad (5)$$

$$pk_1n_1 = (pk_0 + pK_0 + H_0 + d/(p+p_0))n_0. \quad (6)$$

Thus

$$\frac{n_0}{n_1} = R = \left[\frac{k_0 + K_0}{k_1} + \frac{H_0}{pk_1} + \frac{d}{pk_1(p+p_0)} \right] - 1. \quad (7)$$

If thermal equilibrium exists between the 2^3P_0 and 2^3P_1 states

$$k_1 = k_0\alpha = k_0(q_0/q_1)e^{\epsilon/kT}, \quad (8)$$

q_0 and q_1 are the statistical weights of the 2^3P_0 and 2^3P_1 states, respectively. Due to the rapid interchange of atoms between these states, the deviation from thermal equilibrium will be small, especially in the case of nitrogen.

Then from (5), (7) and (8)

$$J = \frac{I}{I_0} = \frac{n_1^{(p)}}{n_1^{(0)}} = \left[1 + \frac{p}{P}K_1 + \frac{p}{P}k_1 \left(1 - \frac{R}{\alpha} \right) \right]^{-1} \quad (9)$$

¹⁶ Magliano and Gaviola, *Univ. Nac. La Plata, Estudio Ciencias* **5**, No. 93, 479 (1931).

(9) is the general expression for the quenching by carbon monoxide and by nitrogen.

(a) For low pressures of the foreign gas—we may for such low gas pressures that diffusion to the walls will destroy most of the 2^3P_0 atoms put $R/\alpha \ll 1$ in (9) and obtain

$$J = [1 + (p/P)(k_1 + K_1)]^{-1}. \quad (10)$$

(b) For high pressures of the foreign gas—neglecting diffusion in (7), the substitution of (7) into (9) gives

$$J = \left[1 + \frac{k_1 k_0 I I_0}{P(k_0 + K_0)^2} + \frac{p}{P} \left(K_1 + \frac{k_1 K_0}{k_0 + K_0} \right) \right]^{-1}. \quad (11)$$

From (10) and (11) the curve of $1/J$ against p is seen to have two straight line portions, one at very low pressures and the other at high pressures, the latter having the smaller slope.

On the basis of the equations given, the values of neither k_1 nor K_1 , but of only $k_1 + K_1$ can be obtained from the experimental data. Samson⁷ found that nitrogen apparently produced the transition $2^3P_1 \rightarrow 1^1S_0$, corresponding to K_1 , with an appreciable probability, but only with stimulated emission of $\lambda 2537$. Such a process would not, therefore, be detected in quenching experiments. On the basis of both this fact and the impossibility, on the basis of any known energy transfer, to attribute to a radiationless transition $2^3P_1 \rightarrow 1^1S_0$, produced by carbon monoxide or by nitrogen, a probability comparable with that of the transition $2^3P_1 \rightarrow 2^3P_0$, K_1 has been neglected in this analysis. The value of k_1 then obtained does not depend upon the assumption of thermal equilibrium between the 2^3P_0 and 2^3P_1 states.

Curves of $1/J$ as a function of p are given in Fig. 7 for carbon monoxide at 473°K and at 973°K and in Fig. 8 for nitrogen at 673°K and 873°K. In Table II are given the values of k_1 , K_0 ,

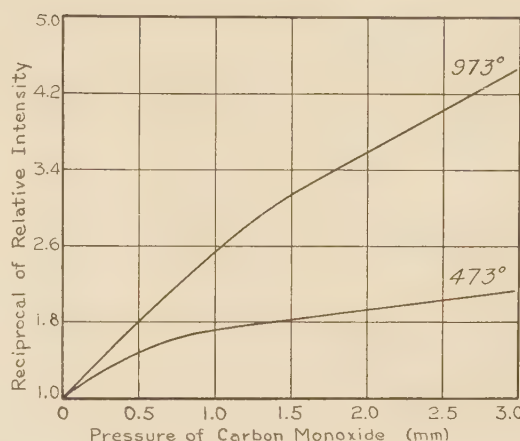


FIG. 7. $1/J$ as a function of the pressure of carbon monoxide.

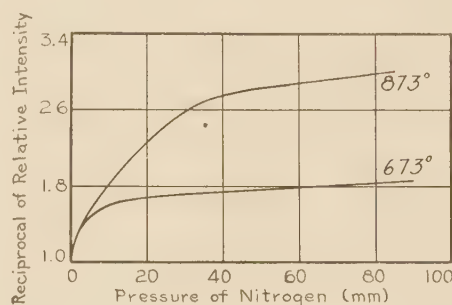


FIG. 8. $1/J$ as a function of the pressure of nitrogen.

and H_0 , obtained from these curves, and of the respective corresponding effective cross sections Σ_1^2 , Σ_0^2 , and S_0^2 . The latter are calculated from the following formulas.⁷

$$k_1 = (2N\sigma_1^2/p)(2\pi kT/\mu)^{1/2}, \quad (12)$$

$$K_0 = (2N\Sigma_0^2/p)(2\pi kT/\mu)^{1/2}, \quad (13)$$

$$H_0 = 2nS_0^2(2\pi kT/\mu)^{1/2}. \quad (14)$$

The values of k_0 and of the corresponding

TABLE II. Constants for the quenching of mercury resonance radiation in CO and N₂.

Gas	T°K	k_1	σ_1^2 cm ²	K_0	Σ_0^2 cm ²	H_0	S_0^2 cm ²
CO	473	3.05×10^6	7.40×10^{-16}	4.62×10^4	1.12×10^{-17}	9.17×10^4	1.60×10^{-16}
	773	2.60	8.06	12.4	3.85	37.1	8.29
	973	1.96	6.82	9.65	3.36	33.0	8.28
N ₂	473	2.52×10^6	6.12×10^{-17}	4.25×10^2	1.03×10^{-19}	3.84×10^4	6.71×10^{-17}
	673	2.73	7.91	6.16	1.78	21.5	44.8
	873	2.52	8.33	6.55	2.16	20.7	49.1

TABLE III. Values of k' and σ_0^2 in the quenching of mercury resonance radiation in CO and N₂.

Gas	T°K	k_0	$\sigma_{0(a)}^2 \text{ cm}^2$	$\sigma_{0(b)}^2 \text{ cm}^2$
CO	473	4.30×10^4	3.49×10^{-16}	7.72×10^{-16}
	773	29.7	5.66	4.84
	973	43.6	5.68	3.62
N ₂	473	3.56×10^3	2.89×10^{-17}	9.59×10^{-16}
	673	18.9	4.98	7.81
	873	41.6	6.39	6.24

effective cross section σ_0^2 are given in Table III. σ_0^2 is calculated from

$$k_0 = (2N\sigma_{0(x)}^2/p)(2\pi kT/\mu)^{\frac{1}{2}}F_{(x)}. \quad (15)$$

The two values of σ_0^2 correspond to the two values as given by (3) and (4), of F . The subscripts to σ_0^2 correspond to those of F .

In the temperature range investigated the values of all of the effective cross sections, with the exception of $\sigma_{0(b)}^2$, and of σ_1^2 for carbon monoxide, for energy transfer at gas collisions tend to increase somewhat with temperature. The probable process H_0 , independent of the gas pressure, is considered to be the combination of a 2^3P_0 and a 1^1S_0 atom into an excited mercury molecule. S_0^2 , corresponding to this process, has apparently a real variation with temperature for which, due to the present incomplete knowledge of the dependence upon the temperature of the rates of bimolecular reactions, no reason can yet be assigned.

Previous investigations¹⁷ have indicated that no simple relationship exists between the dipole character and the electron affinity of a gas and its

¹⁷ Mannkopf, *Zeits. f. Physik* **36**, 315 (1926); Stuart, reference 2; Zemansky, reference 5.

quenching efficiency. The much greater quenching efficiency of carbon monoxide than of nitrogen may probably be accounted for upon the following basis.

(1) The discrepancy Δ between the amount of energy which the mercury atom gives up in the transition $2^3P_1 \rightarrow 2^3P_0$ and that which the gas molecule may take up as vibrational energy is smaller for carbon monoxide (+0.047 volt) than for nitrogen (+0.070 volt). Since kinetic energy must be supplied at collision, σ_1^2 , as defined, intrinsically contains the factor $e^{-\Delta/kT}$. The greater variation with temperature of this factor for nitrogen than for carbon monoxide may account roughly for the difference between the variation with temperature of σ_1^2 for nitrogen and of σ_1^2 for carbon monoxide.

(2) The probability for the destruction of 2^3P_0 atoms by collisions of the second kind with carbon monoxide is very much greater than that with nitrogen.

This explanation accounts also for the greater dependence upon the temperature of the quenching by nitrogen than of that by carbon monoxide.

Calculations have shown that the neglect of the loss of 2^3P_1 atoms by diffusion to the walls could cause a maximum error of only 10 percent in the evaluation of the quenching constants. The random errors in this evaluation may amount to about 15 percent in the case of carbon monoxide and to about 20 percent in the case of nitrogen.

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